

AD-773 976

PLASMA POLYMERIZATION OF SATURATED  
AND UNSATURATED HYDROCARBONS

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Prepared for:

Office of Naval Research

1 December 1973

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Unclassified  
Security Classification

AD773976

DOCUMENT CONTROL DATA - R & D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) Department of Chemical Engineering University of California Berkeley, California 94720		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE Plasma Polymerization of Saturated and Unsaturated Hydrocarbons		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report		
5. AUTHOR(S) (First name, middle initial, last name) H. Kobayashi, A. T. Bell and M. Shen		
6. REPORT DATE December 1, 1973	7a. TOTAL NO. OF PAGES 35	7b. NO. OF REFS 20
8a. CONTRACT OR GRANT NO. N00014-69-A-0200-1053	8b. ORIGINATOR'S REPORT NUMBER(S) Technical Report No. 7	
b. PROJECT NO. NR 356-526		
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.		
10. DISTRIBUTION STATEMENT Approved for public release: Distribution Unlimited		
11. SUPPLEMENTARY NOTES Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE U.S. Department of Commerce Springfield, VA 22151		12. SPONSORING MILITARY ACTIVITY Advanced Research Projects Agency, monitored by Office of Naval Research
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41

**Unclassified**  
**Security Classification**

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
plasma polymerization hydrocarbons glow discharge		1				

AD 773976

ADVANCED RESEARCH PROJECTS AGENCY  
Contract No. N00014-69-A-0200-1053

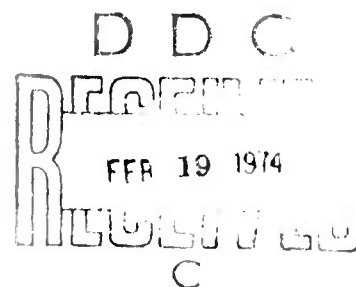
Monitored by  
OFFICE OF NAVAL RESEARCH  
Task No. NR 356-526  
Technical Report No. 7

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December 1, 1973

Prepared for publication in  
Macromolecules



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III

1

## Plasma Polymerization of Saturated and Unsaturated Hydrocarbons

by

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### ABSTRACT

A series of nine saturated and unsaturated hydrocarbons were polymerized by subjecting them to a radiofrequency glow discharge at reduced pressures. It was found that acetylene polymerizes most rapidly, followed by ethylene and butadiene, then by propylene, cis-2-butene and isobutylene. The saturated alkanes: methane, ethane, and propane polymerize most slowly. As shown by previous work, the form of the polymer depends upon the rate of polymerization. Thus very high polymerization rates produce only a powder, intermediate rates produce either a powder or a film, and low rates produce only a film. It was found from carbon-hydrogen analysis that polymers prepared from the alkanes exhibited a greater loss of hydrogen than did those from olefinic monomers. The polymer prepared from acetylene exhibited the least loss of hydrogen. Infrared spectra of the polymers made of ethane, ethylene, and acetylene showed that with increasing monomer unsaturation the polymer contained more double bonds, fewer methylene groups, and a greater tendency to be oxidized after preparation. An examination of the mechanism of ethylene polymerization led to the conclusion

that a significant amount of oligomerization occurs in the gas phase. In addition it is hypothesized that an important initial step is the partial conversion of ethylene to acetylene. This hypothesis can also be extended to the other monomers to explain their relative rates of polymerization.

## INTRODUCTION

There has recently been an increasing interest in the use of low pressure electric discharges for the polymerization of organic and organometallic compounds<sup>1-5</sup>. The formation of a polymer by this means is a complex process which is initiated by collisions between energetic free electrons, present in the plasma formed by the discharge, and molecules of the monomer. The products of these collisions are ions, excited molecules, and free radicals<sup>6</sup>. Once formed these species can react with themselves as well as with additional ground state molecules to produce polymers both in the gas phase as well as on solid surfaces placed in the plasma. Because of its complexity, the mechanism of plasma-polymerization is not well understood. In our previous publications<sup>7,8</sup> dealing with the plasma-polymerization of ethylene, a mechanism was proposed to explain the dependence of polymerization rate and the type of polymer formed on the reaction conditions. In the present work, the investigation is broadened to include a number of saturated and unsaturated hydrocarbon gases. On the basis of their relative rates of polymerization and the characteristics of the corresponding polymers, additional information has been obtained relating to the plasma-polymerization of hydrocarbons.

## EXPERIMENTAL

The detailed experimental arrangement for plasma polymerization has been described previously<sup>7</sup>. The apparatus consists of an evacuable bell jar housing a parallel pair of disc electrodes. An International Plasma Corporation Model PM 401 Radiofrequency Generator was used to sustain the discharge. The generator operates at 13.56 MHz and has a maximum power output of 150 watts. The lower electrode was water cooled. The rate of polymerization was determined by weighing the amount of polymer accumulated on a piece of aluminum foil covering the lower electrode. Monomer gases (CP grade) were purchased from Matheson Chemical Company, and were used as received.

## RESULTS AND DISCUSSION

### Rates of Polymerization

The rates of polymerization in a glow discharge at a pressure of 2 torr and a power of 100 watts are compared in Figure 1 for three saturated hydrocarbons. It is seen that at high monomer flow rates the polymerization rates are fairly constant with increasing flow rate. Here propane has the lowest polymerization rate, ethane has a higher rate and methane still higher. Note that the rates of polymerization are expressed in terms of  $\text{mg/hr-cm}^2$ . If these were expressed on a molar basis, the order of methane > ethane > propane would have been more clearly delineated. This hierarchy is, however, reversed at low flow rates. Of particular interest is the behavior of methane, which has a very gradual increase in polymerization rate with decreasing flow rate. In contrast, polymerization rates increase dramatically for ethane and propane. This difference is probably a consequence of the unique mechanism of methane polymerization, as shall be discussed later.

The polymerization rates of three olefinic hydrocarbons are compared in Figure 2. Here isobutylene polymerizes most slowly, while propylene polymerizes faster throughout the entire range of flow rates. Ethylene, on the other hand, has a polymerization rate that is an order of magnitude greater than either isobutylene or propylene (note the enhanced ordinate scale for ethylene in Figure 2). These data appear to indicate that in a given homologous series of hydrocarbons, higher polymerization rates are favored by lower molecular weights.

Comparison of Figures 1 and 2 shows that for molecules with the same number of carbon atoms, the presence of unsaturation leads to a higher polymerization rate. In addition, Figure 3 shows that for three monomers containing four carbon atoms, butadiene with two double bonds polymerizes substantially faster than either cis-2-butene or isobutylene each of which contains one double bond. To investigate the role of unsaturation one step further, acetylene was polymerized under the same conditions of 2 torr and 100 watts. In this case, the rate was so high that polymer was formed instantaneously not only on electrodes, but also throughout the reactor. In order to more reliably determine the polymerization rate, the pressure was reduced to 0.5 torr and the power to 50 watts. Figure 4 shows that under these conditions acetylene, which contains a triple bond, polymerizes faster than ethylene, which contains a double bond, by more than an order of magnitude. Figure 4 also shows that for identical conditions ethylene polymerizes faster than ethane by an order of magnitude.

Another interesting feature emerging from the comparison of polymerization behavior of ethane, ethylene and acetylene is the existence of maxima in polymerization rates of the latter two monomers (Figure 4). In our previous publication<sup>7</sup>, we have explained this behavior in terms of the competition between the rate of generation of reactive species and the rate of flow of the monomer feed gas. At very low flow rates, where the residence time of the monomer in the plasma is sufficiently high to establish a steady state concentration

of reactive species, polymerization consumes all of the monomer. As the flow rate is increased, the polymerization rate will first increase due to the greater supply of monomer. However, as the flow rate continues to increase, a point is reached where the reactive species are removed so rapidly that the effective residence time for these species is reduced, and the polymerization rate decreases. This mechanism should also hold for ethane and a maximum must also exist in its polymerization rate vs. flow rate curve. The absence of this maximum in Figure 4 is most likely due to the low flow rate at which it occurs. Such a low rate flow/ could not be obtained with the existing equipment. Finally, it should be noted that the position of the maximum polymerization rate for any monomer can be correlated with its relative ease of polymerization. Maxima for the more easily polymerized monomers are located at higher flow rates.

#### Polymer Characterization

The carbon and hydrogen content of each polymer was determined by Pregl's method and the results are summarized in Table 1. All samples were made under the condition of 2 torr pressure, 5 cm<sup>3</sup>/min (STP) flow rate and 100 watts power. The second column of Table 1 shows the experimentally determined values of the number of hydrogen atoms per carbon atom in the polymers. For the sake of comparison, H/C ratios for the original monomers are given in the third column. The fourth column lists values of the H/C ratio for each polymer divided by that of the monomer.

The general conclusion one can immediately draw from Table 1 is that each of the polymers is hydrogen-deficient by comparison with its respective monomers. Acetylene, however, has almost the same number of hydrogens per carbon atom as the monomer, and can be considered unique among all the hydrocarbons investigated here. The second group of polymers that are approximately 10-30% hydrogen-deficient are produced from double bond containing monomers, with butadiene leading the list. Finally, polymers derived from alkanes are found to be the most hydrogen-deficient, with only about half as many hydrogen atoms per carbon atom in the polymer as in the monomer.

The observed hydrogen deficiency suggests that the polymers are very highly crosslinked three dimensional networks containing significant amounts of unsaturation. Further confirmation of these characteristics was obtained from measurements of solvent swelling and infrared spectra.

It is well known that linear amorphous polymers will dissolve in appropriate solvents but that crosslinked polymers only exhibit swelling. The degree of swelling decreases with increasing degree of crosslinking, until at very high crosslink densities no swelling is detectable. Attempts to dissolve or swell the rigid polymer films and powders made during this study in boiling m-xylene, a common solvent for parafins, were unsuccessful. Oily films, however, were soluble because of their very low molecular weight<sup>8</sup>.

Infrared spectra of the polymers produced from acetylene, ethylene, and ethane are shown in Figure 5. The absence of the  $\text{CH}_2$  rocking band at  $730\text{ cm}^{-1}$  normally observed in crystalline parafins indicates that these polymers are amorphous. We have also noted previously that plasma-polymerized ethylene shows no evidence of crystallinity by x-ray diffraction.

The spectrum shown in Figure 5a exhibits a strong peak at  $1600\text{ cm}^{-1}$ , which is due to vibrations of the  $\text{C}=\text{C}$  bond. This peak is weaker in Figure 5b, and is almost undetectable in Figure 5c. On the other hand, the peak intensities at  $2960\text{ cm}^{-1}$  ( $\text{CH}_2$  stretching),  $1463\text{ cm}^{-1}$  ( $\text{CH}_2$  bending), and  $1369\text{ cm}^{-1}$  ( $\text{CH}_2$  wagging) are very strong in Figures 5b and 5c, but much weaker in Figure 5a. These observations suggest that the plasma-polymerized acetylene contains mainly double bonds in the chain, ethane contains mainly single bonds with a structure not unlike a highly crosslinked polymethylene, while the plasma-polymerized ethylene has an intermediate structure.

Another interesting feature one notes in these spectra is that the peak at  $3400\text{ cm}^{-1}$  for OH stretching is very strong for plasma-polymerized acetylene. But the same peak is much weaker for plasma-polymerized ethylene and nearly undetectable for plasma-polymerized ethane. The  $\text{C}=\text{O}$  stretching frequency at  $1700\text{ cm}^{-1}$  also follows this trend. The presence of these functional groups is most likely due to a partial oxidation of the polymer surface after its preparation. The reactions with atmospheric oxygen are more extensive for acetylene and ethylene polymers probably because their double bonds are more

susceptible than the single bonds in the ethane polymer.

#### Powder and Film Formation

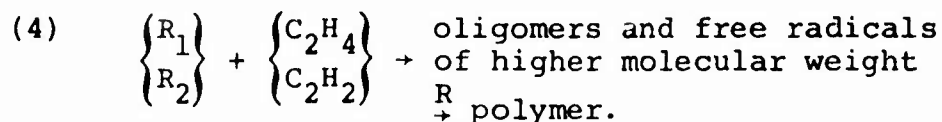
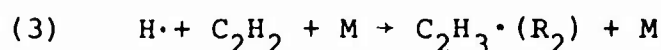
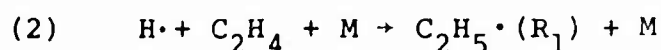
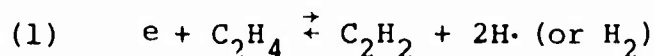
We have already shown in previous publications<sup>7-9</sup> that the form of the polymers produced by the plasma-polymerization of ethylene depends strongly on the reaction conditions. Figure 6 illustrates a "characteristic map" for the plasma polymerization of this monomer. It is shown here that the polymer may be a powder at low pressure and low flow rate, a colorless rigid film at low pressure and high flow rate, and an oily film at high pressure and high flow rate. The discharge becomes unstable in the region of high pressure and low flow rate. Also shown in Figure 6 is the characteristic map for the plasma polymerization of ethylene mixed with 22% of acetylene. As we shall see presently, the effect of introducing acetylene is to increase polymerization rate. For the more rapidly polymerizing systems, both the regions of powder formation and unstable discharge are enlarged while the film formation region is reduced. The trend appears to hold for all of the hydrocarbon monomers investigated in this work. Thus pure acetylene, which polymerizes extremely vigorously, forms only a powder over the region of pressure and flow rate for which polymerization is possible (Figure 7). Butadiene, which polymerizes at a rate comparable to ethylene, forms a powder at low flow rates and a film at high flow rates, as does ethylene. Propylene, isobutylene, and cis-2-butene polymerize more slowly. These monomers form rigid films at

high flow rates but oily films at low flow rates. The alkanes which polymerize slowly under all conditions form only rigid films.

The characteristic map for acetylene in Figure 7 requires further comment. The only conditions under which polymers are produced are those located in the shaded region. At low flow rates the polymerization rate is so high that all of the monomer is converted instantaneously and therefore it becomes impossible to maintain the monomer pressure. The broken line indicates the lowest pressures achievable by the pump when unreacted monomer gas is fed at various flow rates. This limit is extended when the discharge is on, since the rapid polymerization reaction acts as an additional pump. At higher pressures, the discharge is unstable. Under these conditions the glow covers only a portion of the electrodes and moves from one position to another in an irregular manner. It is believed that the presence of powder particles in the gas phase is closely connected to the onset of the unstable operation. This connection is based on the observation that a large quantity of particles in the gas can act as an electron sink making it harder to sustain the discharge<sup>10</sup>. Correspondingly, acetylene, which forms powder exclusively, is characterized by a large unstable region. This unstable region is much smaller for ethylene (Figure 6), whose polymerization rate is slower than that of acetylene by an order of magnitude. Finally, the alkanes which polymerize very slowly and do not produce a powder product show no evidence of unstable operation.

### Polymerization Mechanism

Since the process of plasma-polymerization is quite complex, it has not yet been possible to work out a complete mechanism for any monomer. Never-the-less some progress has been made towards this end. In a recent study<sup>8</sup>, we have proposed that the plasma-polymerization of ethylene proceeds by the mechanism outlined below.



The critical part of this mechanism is reaction 1 which leads to the formation of acetylene and hydrogen atoms. The hydrogen atoms thus formed are assumed to react with both acetylene and ethylene to produce free radicals which in turn lead to the formation of polymer. Alternatively the hydrogen atoms may convert the acetylene back into ethylene. An effort to substantiate the importance of reaction 1 was undertaken as a part of this study.

To investigate the degree to which gas phase polymerization of ethylene does occur, the composition of the effluent gas from the reactor was analyzed by a mass spectrometer. For this work an evacuated ampoule was attached to the line between the reactor and the vacuum pump. Fifteen minutes after the

discharge was turned on the ampoule was filled with the effluent gas and sealed. The contents of the ampoule were subsequently analyzed on a CEC-110B high resolution mass spectrometer.

Figure 8 illustrates the mass spectroscopy results as a function of the extent of the ethylene monomer converted to polymer. Three curves are shown, one for ethylene (mass number 28), a second for acetylene (mass number 26), and a third representing all species whose mass to charge ratio is greater than 35. We note at once that acetylene is present even at low degrees of conversion and to an extent which is greater than that observed in the cracking pattern of ethylene alone. As the extent of conversion increases the concentrations of ethylene and acetylene both fall while bearing a nearly constant ratio to each other. By contrast, the concentrations of higher molecular weight species increase with increasing monomer conversion. The implication of these results is that part of the ethylene is rapidly converted to acetylene and that both ethylene and acetylene can lead to the appearance of higher molecular weight species in the gas phase (n.b. the highest value of  $m/e$  observed was 100). These high molecular weight species are considered to be the precursors to the final polymer (see reaction 4).

In-as-much as it had been observed that acetylene polymerizes much more rapidly than ethylene under identical conditions (see Figure 4), it was of interest to determine whether the principal source of polymer obtained during the

polymerization of ethylene might not be the acetylene derived via reaction 1. To examine this point further the rate of polymerization was measured for premixed mixtures of ethylene and acetylene. During these experiments the total flow rate was maintained constant thereby producing a constant residence time for both ethylene and acetylene. As may be seen from Figure 9, initially the rate of polymerization increases linearly with increasing content of acetylene in the monomer mixture and the only product formed is a film. Above 30 volume percent of acetylene, the rate rises more rapidly and powder is formed in addition to the film. A similar pattern is observed if ethane is substituted for ethylene. A significant observation is that the slopes of the linear portions of the curves in Figure 9 are nearly identical for ethane and ethylene, about  $0.3$  to  $0.4 \text{ mg/cm}^2\text{-hr}$  per 10 volume percent of acetylene. This corresponds to about a 20% conversion of the acetylene in the monomer mixture. Based upon this evidence we may hypothesize that the added acetylene polymerizes independently of the comonomer (i.e., ethylene or ethane) and that when ethylene alone is used as the monomer its polymerization rate is governed by the amount of acetylene formed via processes such as reaction 1.

Additional substantiation of the proposed reaction scheme was obtained by the addition of hydrogen to a constant supply of ethylene (partial pressure was maintained at 2 torr). The effects of hydrogen on both the polymerization rate and the hydrogen content of the polymer are shown in Figure 10. That

the polymerization rate decreases with increasing hydrogen flow rate leads us to the hypothesis that the added hydrogen causes the acetylene formed by reaction 1 to be converted back to ethylene. A partial conversion of ethylene to ethane is also expected. The net decrease in the level of unsaturation of the gas phase brought about by these changes would explain the decrease in polymerization rate and the increased hydrogen content of the polymer.

Figure 11 illustrates the results of another experiment, in which argon was added to a constant flow of ethylene. In this instance the rate of polymerization is seen to increase with increased argon flow rate. This effect is believed to be due to collisions between argon metastables and ethylene molecules leading to the production of additional acetylene beyond that obtained via reaction 1. The ability of argon metastables to bring about a loss of hydrogen is demonstrated by the reduced hydrogen content in the polymer produced at higher argon flow rates.

The insights into the mechanism of ethylene polymerization developed above also provide an understanding for the relative rates of polymerization of the other monomers. As was noted in the discussion of Figures 1-4 the rate of polymerization can clearly be correlated with the degree of unsaturation present in the monomer molecule. If one again assumes that in order to obtain polymerization it is necessary to first convert a part of the monomer into acetylene, then the greater the unsaturation of the monomer, the easier it will be to

obtain acetylene from it. Table 2 compares the mass spectra of the monomer and the gaseous effluent for discharges sustained in acetylene, ethylene, ethane, and butadiene. Two points can be made based upon this table. The first is that the spectrum of the effluent gas in every case shows the presence of substantial amounts of species with values of  $m/c$  between 35 and 100 which are negligible in the spectrum of the monomer. This is further evidence in support of the assumption that a certain extent of the polymerization occurs in the gas phase. The second point is that the ratio of acetylene present in the effluent gas, which does not derive from cracking of the monomer in the mass spectrometer, to monomer correlates fairly well with the observed polymerization rates. This observation supports the original proposition.

A mechanism for formation of acetylene can be proposed by analogy with what is observed during photolysis of the monomer. Table 3 summarizes the elementary reactions assumed to be responsible for the formation of acetylene. The column marked references refers to the photolysis literatures upon which the mechanisms are based. From Table 3 it is seen that ethylene should form acetylene by direct electron collision. In the case of butadiene, cis-2-butene, and propylene the product of electron collision is a free radical which can rearrange to form acetylene. Isobutylene is also expected to form a free radical upon initial electron collision but the structure of this radical is such that acetylene cannot be formed from it directly. Instead a second electron collision is required.

Ethane and propane are both capable of forming acetylene by a process requiring two electron collisions. The conversion of methane into acetylene is unique in that the product of the first step is a diradical. This diradical in turn reacts with a second molecule of methane to form an excited ethane molecule which decomposes to give a free radical. This last radical then rearranges to give acetylene. Here again it can be observed that the ease with which acetylene can be derived from the monomer correlates very closely with the relative rates of polymerization.

#### ACKNOWLEDGEMENT

This work was supported in part by the Advanced Research Projects Agency of the Department of Defense, monitored by the Office of Naval Research under Contract No. N00014-69-A-0200-1053.

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TABLE 1 Carbon-Hydrogen Ratios of  
Plasma-Polymerized Hydrocarbons

Compound	H/C Ratio Polymer	H/C Ratio Monomer	$\frac{\text{H/C (Polymer)}}{\text{H/C (Monomer)}}$
Acetylene	0.95	1.00	0.95
Ethylene	1.49	2.00	0.75
Propylene	1.40	2.00	0.70
Isobutylene	1.44	2.00	0.72
Cis-2-Butene	1.34	2.00	0.67
Butadiene	1.33	1.50	0.88
Methane	2.40	4.00	0.60
Ethane	1.55	3.00	0.52
Propane	1.58	2.67	0.59

TABLE 2A Mass Spectra of Effluent Gas

m/e	C <sub>2</sub> H <sub>2</sub>		C <sub>2</sub> H <sub>4</sub>		C <sub>2</sub> H <sub>6</sub>		C <sub>4</sub> H <sub>6</sub>	
	monomer	0.5 Torr 40 cm <sup>3</sup> /min 50W	monomer	2.0 Torr 40 cm <sup>3</sup> /min 100W	monomer	2.0 Torr 40 cm <sup>3</sup> /min 100W	monomer	2.0 Torr 40 cm <sup>3</sup> /min 100W
22								
23								
24	4.0	3.2	0.6	0.9	0.3	0.3	0.1	0.3
25	13.8	11.0	2.0	3.9	1.5	1.4	0.9	0.9
26	65.5	59.8	10.4	18.1	9.3	9.1	4.9	6.6
27	1.5	1.6	11.3	12.4	13.3	12.4	11.0	7.9
28	0.2	0.5	51.3	21.5	44.8	41.7	9.6	4.8
29	0.2	0.2	0.9	3.8	11.4	12.4	0.2	1.5
30	0.1	0.1	0.6	0.6	15.9	14.9		0.4
31	0.1			0.1	0.4	0.4		0.1
32								
33				0.1				0.1
34								
35								
36-47	1.4	2.9		17.6	1.1	4.6	24.7	23.7
48-59	1.2	10.5		9.1		0.7	46.8*	42.5*
>60		3.2		8.4		0.4	18.6*	13.6*
								10.5

\* m/e = 54

TABLE 2B Comparison of  $C_2H_2$  Mass Spectra Intensities  
and Polymerization Rates

	$C_2H_2$	$C_2H_4$	$C_2H_6$	$C_4H_6$
$C_2H_2$ content* (%)	91.3	13.7	0.4	3.1
polymerization rate (mg/cm <sup>2</sup> /hr)	3.95	1.29	0.053	1.14
polymerization conversion (%)	51	15	0.6	7.2

\* Defined as  $I_{C_2H_2} \cdot \frac{100}{I_{C_2H_2}^0}$  for  $C_2H_2$  and

$$(I_{C_2H_2} - I_{mon}) \frac{I_{C_2H_2}^0}{I_{mon}^0} \text{ for all other monomers}$$

where  $I$  designates the intensity of the mass spectral peak in the effluent gas and  $I^0$  the peak intensity for the monomer.

TABLE 3 Mechanisms for the Formation of Acetylene

<u>Monomer</u>	<u>Mechanism</u>	<u>Ref.</u>
Ethylene	$e + C_2H_4 \rightarrow C_2H_2 + 2H \text{ or } H_2$	11,12
Butadiene	$e + C_4H_6 \rightarrow 2C_2H_3^\cdot$ $C_2H_3^\cdot \rightarrow C_2H_2 + H^\cdot$ or $e + C_4H_6 \rightarrow C_2H_2 + C_2H_4^*$ $C_2H_4^* \rightarrow C_2H_2 + 2H^\cdot \text{ or } H_2$	13
Cis-2-butene	$e + CH_3CHCHCH_3 \rightarrow C_2H_2 + C_2H_6$	—
Propylene	$e + C_3H_6 \rightarrow C_2H_3^\cdot + CH_3^\cdot$ $C_2H_3^\cdot \rightarrow C_2H_2 + H^\cdot$	12,14
Isobutylene	$e + (CH_3)_2CCH_2 \rightarrow CH_3\dot{C}CH_2 + CH_3^\cdot$ $CH_3\dot{C}CH_2 \rightarrow CH_4\dot{C}H$ $e + CH_4\dot{C}H \rightarrow C_2H_2 + CH_3^\cdot$	—
Methane	$e + CH_4 \rightarrow CH_2: + H_2$ $CH_2: + CH_4 \rightarrow C_2H_6^*$ $C_2H_6^* \rightarrow CH_3CH^\cdot + H^\cdot$ $CH_3CH^\cdot \rightarrow C_2H_4^*$ $C_2H_4^* \rightarrow C_2H_2 + H_2$	15-17
Ethane	$e + C_2H_6 \rightarrow C_2H_4 + H_2$ $e + C_2H_4 \rightarrow C_2H_2 + H_2$	18,19
Propane	$e + C_3H_8 \rightarrow C_2H_4 + CH_4$ $e + C_2H_4 \rightarrow C_2H_2 + H_2$	18,20

## FIGURE CAPTIONS

Figure 1: Rates of plasma polymerization of alkanes as a function of monomer flow rate. (pressure 2 torr; power 100 watts).

Figure 2: Rates of plasma polymerization of olefins as a function of monomer flow rate. (pressure 2 torr; power 100 watts).

Figure 3: Rates of plasma polymerization of butadiene, cis-2-isobutene and isobutylene as a function of monomer flow rate. (pressure 2 torr; power 100 watts).

Figure 4: Double logarithmic plot of rates of plasma polymerization of acetylene and ethylene as a function of monomer flow rate.

Figure 5: Infrared spectra of plasma polymerized hydrocarbons: (a) acetylene, (b) ethylene and (c) ethane.

Figure 6: Characteristic map for the plasma polymerization of ethylene (broken line), and ethylene mixed with 22 volume percent acetylene (full lines). (power 100 watts).

Figure 7: Characteristic map for the plasma polymerization of acetylene. (power 50 watts).

Figure 8: Mass spectroscopic data from the reactor effluent gas in the plasma polymerization of ethylene as a function of conversion. Mass number 26 refers to acetylenic species, 28 ethylenic species and those above 35 polymeric species.

Figure 9: Changes in rates of plasma polymerization of ethylene and the chemical composition of plasma-polymerized ethylene as a function of hydrogen addition. (power 100 watts, monomer flow rate 80 cm<sup>3</sup>/min STP and/pressure 2 torr).  
monomer partial

Figure 10: Changes in rates of plasma polymerization of ethylene and chemical composition of plasma-polymerized ethylene as a function of argon addition. (power 100 watts, monomer flow rate  $80 \text{ cm}^3/\text{min}$  STP and total pressure 2 torr).

Figure 11: Rates of plasma polymerization of ethane and ethylene as a function of acetylene addition. (power 100 watts, monomer flow rate  $90 \text{ cm}^3/\text{min}$  and pressure 2 torr).

